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Article

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Electron-induced Chemistry: Preliminary Comparative Studies of Hydrogen Production from Water, Methanol and Diethyl Ether.

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Abstract

Binary, layered ices comprising of benzene (C_6H_6) on water (H_2O), on methanol (CH_3OH) and on diethyl ether ($CH_3CH_2OCH_2CH_3$) have been irradiated with 250 eV electrons. Molecular hydrogen (H_2) production is observed by quadrupole mass spectrometry to be competitive with (in the case of H_2O), and dominate over (in the case of the organic substrates), C_6H_6 desorption. While very preliminary, these results suggest that chemical change (in the form of dehydrogenation) induced by interaction of organic-rich icy solids with ionising particle radiation may significantly contribute to hydrogen recycling in cold dense environments.

Keywords

Icy grains, molecular clouds, non-thermal desorption, electron-induced chemistry, water ice, solid methanol, solid diethyl ether

Introduction

Solid water is highly abundant in astrophysical environments being one of the main components if not the dominant species in icy mantles coating interstellar dust grains,[1] comets[2] and in icy planetary bodies such as Europa[3,4] where exposure to ionising radiation is a significant promoter of physical and chemical change. Laboratory studies have reported on the effect of electrons, ions and electromagnetic radiation on the physics and the chemistry of H_2O ices; highlighting the species produced and the mechanisms by which these species are formed;[5–8] phase changes;[9–12] and desorption of neutral or ionic species during the irradiation.[13,14]

In astronomical environments, H_2O is always found in the presence of other species. Hence, increasing attention is being paid to understanding the processes taking place after photolysis and radiolysis of other simple pure molecular solids, such as carbon monoxide (CO), ammonia (NH_3), methanol (CH_3OH), acetonitrile (CH_3CN), and their mixtures with H_2O and each other at cryogenic temperatures.[15–25] The results clearly point to a significant role for ion, electron and photon induced chemistry in the formation of complex organic molecules (COMs) in these environments.[26–30] Illustrative is the work of Mason and co-workers on electron bombardment of thin CH_3OH films at 14 K;[31] wherein the reaction products and their yields seem to be independent of the primary electron energy suggesting that the observed electron-induced chemistry (EIC) is linked to the production of low energy secondary excitations within the ice. The authors conclude with the hypothesis that these secondary excitations might represent a common underpinning for irradiation phenomena.

Layered ices are a convenient system to investigate how the aforementioned excitations behave in the interfacial or selvedge regions of a thin film in comparison to the bulk.[32,33] In

such regard, Akin et al. have studied the electron-promoted desorption (EPD) of molecular products from multilayer films of amorphous solid water (ASW) capped with sub-monolayer quantities of CH_3OH at 50 K.[34] They have shown that the EIC in H_2O films is quenched by the CH_3OH adlayers consistent with reactions occurring at the ASW/vacuum interface rather than in the bulk. In this context, we have previously studied C_6H_6 desorption from H_2O, CH_3OH and $CH_3CH_2OCH_2CH_3$ surfaces when irradiated with 250 eV electrons[35,36] These systems were chosen in order to understand the role of hydrogen bonding in transporting electronic excitation within the solid state to the vacuum interface promoting physicochemical change. In essence, we have reduced the degree of hydrogen bonding in the substrate film and possibly between C_6H_6 and the substrate by substituting the hydrogen atom (H) for an alkyl group, while potentially retaining the electronic excited states localised around the O-atom that might ultimately lead to efficient electron promoted desorption (EPD) of C_6H_6 from solid H_2O. This is not observed for the organic-based substrates (CH_3OH and $CH_3CH_2OCH_2CH_3$), where EPD is a minor process.

This leads us to ask what other processes are favoured over C_6H_6 desorption? How do these processes relate to the different chemical nature of the three binary ices? In order to assess these open questions, we present electron irradiation experiments of binary ices comprising sub-monolayer quantities of C_6H_6 on top of $H_2O/CH_3OH/CH_3CH_2OCH_2CH_3$ and compare EPD versus our preliminary observations on electron-induced H_2 formation.

Experimental

The experiments discussed here were performed in a stainless steel UHV chamber with a base pressure in the chamber of $2 < 10^{-10}$ Torr at room temperature as it has been described in detail elsewhere.[37,38] The substrate is a polished stainless steel disk cooled by thermal contact with a liquid nitrogen reservoir giving a base temperature of 109 ± 2 K. The substrate was resistively heated up to 600 K for 15 minutes to remove volatile contaminants before cooling

prior to conducting experiments each day.

Layered ices were obtained by sequential background deposition using two independent manifolds for C_6H_6 (Fluka 99.5% pure), and for de-ionised H_2O, CH_3OH (Sigma-Aldrich, HPLC grade 99.9% pure), or $CH_3CH_2OCH_2CH_3$ (Sigma-Aldrich, Chromasolv grade 99.9% pure). All the chemicals were stored in separate glass vials and were further purified by several freeze-pump-thaw cycles before use. Exposure is reported in Langmuir ($1L = 10^{-6}$ Torr s). Film thickness, d, can be estimated from (Eq. 1):

$$d = \frac{SPt}{\sqrt{2\pi m k_B T}} \frac{1}{\rho_s} = \frac{Z_W t}{\rho_s} \quad (1)$$

where S is the sticking coefficient assumed to be 1, P is the ion gauge pressure reading corrected for using appropriate relative sensitivities,[36,39–42] t is the time of exposure, k_B is the Boltzmann constant, T is the temperature for the dosed molecules, Z_W is the bombardment rate (the incident flux), and m is the molecular mass. The molecular volume density, ρ_S, was assumed to be 2.74×10^{22} molecule cm^{-3}, 1.91×10^{22} molecule cm^{-3}, 5.80×10^{21} molecule cm^{-3} and 8.57×10^{21} molecule cm^{-3} for H_2O, CH_3OH, $CH_3CH_2OCH_2CH_3$[a], and C_6H_6 respectively.[43–48]

Desorption of molecular species during electron irradiation at 250 eV was followed by a crossed-beam source, quadrupole mass spectrometer (VG Microtech PC300D, further modified by European Spectrometry Systems) with a homemade line-of-sight tube facing the front of the sample. Sample irradiation was performed using an electron gun (Kimball Physics, ELG-2) incident at ca. 30° with respect to the substrate normal and over an area of 1 mm^2. The resulting average electron flux was $(9 \pm 2) \times 10^{13}$ electron cm^{-2} s^{-1}. Our previous work on the same ices,[36] consistent with the experimental conditions reported herein, showed that in all the systems investigated, the solid films have an overall thickness (> 12 nm) greater than the calculated electron maximum penetration depth (7-9 nm).

[a]Density of the liquid phase, Sigma-Aldrich

Results and discussion

The upper panels of Figure 1 report the electron-promoted desorption (EPD) of C_6H_6 from solid H_2O, CH_3OH and $CH_3CH_2OCH_2CH_3$ surfaces.

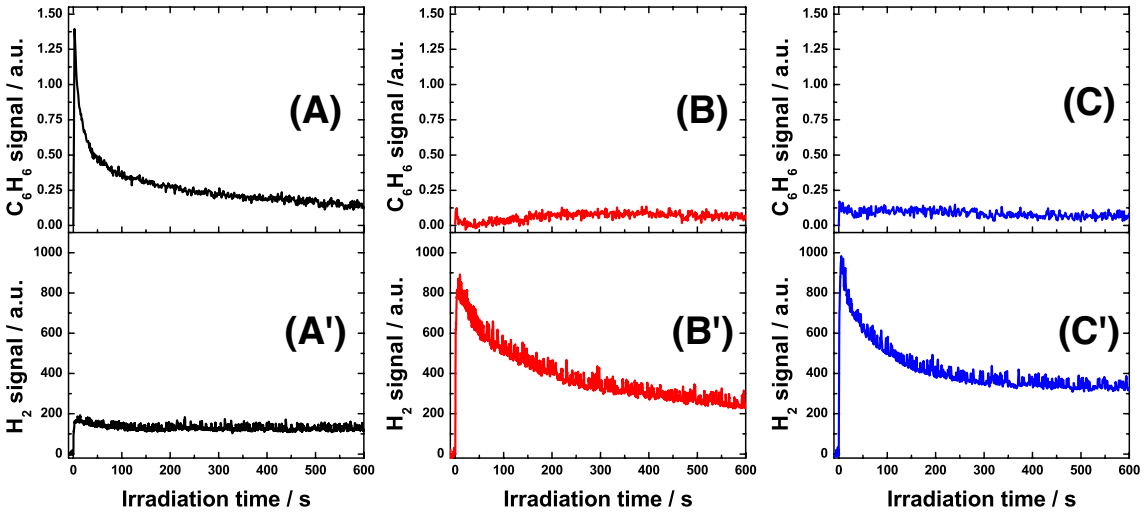

Figure 1: Upper panels: C_6H_6 EPD signal obtained for 5 L (0.2 nm thick in average) of C_6H_6 on a thick ice of ASW, in black (A), of CH_3OH in red (B), and of $CH_3CH_2OCH_2CH_3$, in blue (C). Irradiation starts at t=0 s with 250 eV electrons. Lower panels: H_2 formation detected obtained during irradiation of 1 L of C_6H_6 on a thick ice of ASW (150 L; 18 nm) in black (A′), of CH_3OH (250 L; 19 nm) in red (B′), and of $CH_3CH_2OCH_2CH_3$ (500 L; 30 nm) in blue (C′). Irradiation starts at t=0 s with 250 eV electrons. The intensities have been scaled by the same factor used for the plots in the upper panels for ease of comparison

As discussed elsewhere,[35,36,49] these results indicate that non-thermal desorption of the C_6H_6 adsorbate is not significant from the CH_3OH and $CH_3CH_2OCH_2CH_3$ substrates, in contrast to H_2O. It follows that the energy deposited during the irradiation with 250 eV electrons is directed towards other, perhaps more chemical, outcomes. In fact, we noticed that, as soon as the irradiation began, the base pressure inside the chamber increased almost an order of magnitude for a few minutes. In comparison, the base pressure remained almost unchanged while irradiating the C_6H_6/ASW system or relatively thick films of C_6H_6 (*e.g.* 50 L) regardless the substrate (data not shown). This observation is incompatible with EPD of C_6H_6, given the low signal-to-noise ratio of the data (Figure 1, panels B and C), and points unequivocally towards different processes occurring on and in CH_3OH and

$CH_3CH_2OCH_2CH_3$ ices. We would like to stress that a detailed understanding of the reactive processes involved is beyond the scope of this letter. Simply, we wish to address the following questions: what is the dominant process occurring upon irradiation of C_6H_6/CH_3OH, and $C_6H_6/CH_3CH_2OCH_2CH_3$? Furthermore, if this process is also observable for C_6H_6/ASW, how does it relate to EPD of C_6H_6?

Preliminary experiments of controlled and slow sublimation of the irradiated ices are consistent with the detection of complex organic molecules (COMs) as previously identified by Kaiser and co-workers.[15,16] These species are likely to be formed also during the irradiation of $CH_3CH_2OCH_2CH_3$ films along with many other products given the high reactivity of ethers. The numerous studies on non-thermal reactions in condensed phases stimulated by charged particles and energetic photons, particularly those on solid CH_4[50,51] and H_2O,[8,14,52] provide us with the means to readily identify molecular hydrogen (H_2) formation-desorption as the main process which satisfies two essential requirements: 1) it is relevant to the three investigated systems; 2) it is in common for all of the binary ices reported in this work.

Therefore, we have repeated the three key experiments in Figure 1 and performed 250 eV electron irradiation experiments on binary layered systems comprised of 1 L of C_6H_6 adsorbed on thick ices of ASW, CH_3OH or $CH_3CH_2OCH_2CH_3$; but this time the aim was to observe volatile reaction products, particularly H_2 which is formed in large quantities in all the investigated systems. The lower panels of Figure 1 displays the EIC curves obtained by plotting the mass spectrometer ion signal at $\frac{m}{z} = 2$ as a function of irradiation time for C_6H_6/ASW, C_6H_6/CH_3OH and $C_6H_6/CH_3CH_2OCH_2CH_3$. The most striking aspect is that the average intensity of the recorded traces is several orders of magnitude larger than the intensity of the EPD curves. This is particularly evident for C_6H_6/CH_3OH and $C_6H_6/CH_3CH_2OCH_2CH_3$ where non-thermal desorption of the adsorbed C_6H_6 is negligible.

The moment irradiation begins, a prompt rise in the recorded traces is noted. The increase in H_2 signal intensity is larger for CH_3OH and $CH_3CH_2OCH_2CH_3$ ices and clearly smaller for ASW in a manner consistent with the qualitative observations on the change in

the chamber base pressure. Furthermore, it is noticeable from Figure 2 that the curve C′

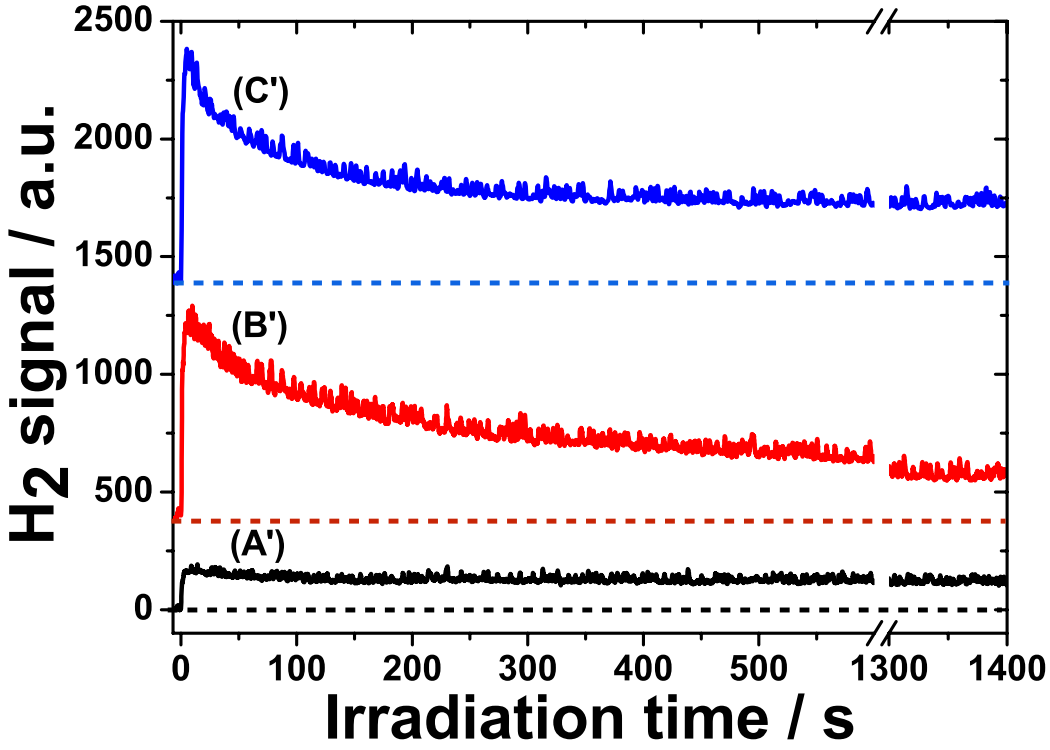

Figure 2: H_2 formation detected obtained during irradiation of 1 L of C_6H_6 on a thick ice of (A′) ASW in black (150 L), (B′) CH_3OH in red (250 L), and (C′) $CH_3CH_2OCH_2CH_3$ in blue (500 L). These are the same experiments shown in Figure 1, but over a longer time scale. Irradiation starts at t=0 s with 250 eV electrons. EIC traces have been offset for clarity with the dashed lines showing the zero lines for each curve. The intensities have been scaled by the same factor used in Figure 1 for ease of comparison.

reaches a plateau around 400 s, and will eventually decrease to zero at very long time of exposure to the beam. In contrast, curve B′ slowly but continuously decays during the whole experiment. This difference between the EIC traces can be primarily linked to the higher density of C-H bonds per molecule in the irradiated volume, which can be broken releasing H atoms. A complementary argument would be that a thicker $CH_3CH_2OCH_2CH_3$ film (*ca.* 30 nm) will result in a long-lived steady state of H_2 formation compared to the thinner CH_3OH ice (*ca.* 19 nm). More studies are required to understand the different decay behaviour of C′ and B′ at long irradiation times (*e.g.* $>$ 1000 s). Pragmatically, it is clear from curves C′ and B′ in Figure 2 that there is still a significant amount of H_2 desorption above 1000 s,

hence indicating the presence of an icy film not fully depleted in the irradiation area.

Integrating each EIC curve up to 600 s (see Figure 1) allows estimates of the gross yield of H_2 to be made, namely $\Phi_{600}(H_2O)$, $\Phi_{600}(CH_3OH)$, and $\Phi_{600}(CH_3CH_2OCH_2CH_3)$, and permits a semi-quantitative comparison among the three systems. The ratio between the area obtained for curves B′ and A′, $\Phi_{600}(CH_3OH)/\Phi_{600}(H_2O)$, gives a value of 2.9 ± 0.3, while taking into account the H_2 formed in $C_6H_6/CH_3CH_2OCH_2CH_3$ (curve A′) with respect to the analogous system with ASW (curve A′), we obtain a ratio $\Phi_{600}(CH_3CH_2OCH_2CH_3)/\Phi_{600}(H_2O)$ of 3.2 ± 0.4. In conclusion, the EIC trace labelled A′ provides evidence of less H_2 formation while irradiating C_6H_6/H_2O with 250 eV electrons, and appears to be roughly constant in time after 100 s. In contrast, C′ and B′ display a significant increase of the signal as soon as the electron beam is turned on, and their exponential decay is still noticeable after 100 s.

In the series experiments represented by Figure 1, irradiation is performed on binary layered ices with 1 L of C_6H_6 as adlayer in order to allow direct comparison with the EPD curves.[36] For now we cannot rule out the possibility that the observed EIC traces contain a contribution from both the underlying substrate and from the C_6H_6 adlayer. However, direct dehydrogenation of C_6H_6 can be discarded because we noted a negligible variation of the base pressure (data not shown) during the irradiation of large C_6H_6 doses (*e.g.* $>$ 20 L). Moreover, if substrate-mediated dehydrogenation of C_6H_6 were to be important we would expect to see a noticeably more intense signal for the C′ trace than for B′ curve in the first moments of irradiation because of the larger contact area at the interface for $C_6H_6/CH_3CH_2OCH_2CH_3$ than for C_6H_6/CH_3OH.[53] Therefore, we think that the EIC signal displayed in Figure 1 refers to H_2 production mainly, if not almost exclusively, from the H_2O, CH_3OH and $CH_3CH_2OCH_2CH_3$ films.

The origins of H_2 from ASW is well-described in our recent publications[35] and rests on the extensive work of Kimmel and co-workers.[54] Briefly, electronic excitations of the O-atom lying in the 8.7-14.5 eV range[55,56] are compatible with the energy distribution of the secondary electrons produced during the irradiation and result in the formation of excitons in

the ASW film. These long-lived excitons migrate to the C_6H_6 (and vacuum) interface *via* the hydrogen-bonding network in the solid H_2O resulting in electronically excited H_2O molecules. These, at the C_6H_6 interface, (i) could promote H_2O desorption or bond cleavage leading to H_2 formation and desorption or (ii) could transfer the excitation to the hydrogen-bonded aromatic ring enabling its desorption.

In contrast, the replacement of the H-atoms in the H_2O molecule with alkyl groups, which contain C-atom(s), has a two-fold impact. The degree of H-bonding is significantly reduced in the solid underlying the C_6H_6 which will hinder the excitation transfer from the bulk to the interfaces where desorption can be promoted. The presence the C-atom(s) introduces another electron-rich centre in the molecule that lowers the ionisation potential[35,36,57,58] by adding an additional spectrum of electronic excitations. This might favour other processes over desorption, channelling the secondary electronic excitations towards reactive routes. This is consistent with 5 keV electron irradiation experiments of pure methane (CH_4) ices at 10 K which clearly show that the predominant reaction pathway is the homolytic cleavage of the C-H bond.[50] The H atoms, free to diffuse in the ice matrix, will subsequently combine to form H_2 which then desorbs. Therefore, the EIC curves in Figure 1, labelled as C′ and B′ are consistent with the idea that electrons will mainly promote dehydrogenation over physical processes such as EPD for organic-based ices.

It is important to stress that the observed EIC traces are the result of several competitive processes taking place in parallel during the electron irradiation. Hence, their kinetics will be identical. Further work is clearly required to address more fully the nature of the gas phase products from energetic processing of especially ices rich in organic material and to investigate the effect of the ice temperature on the observed processes.

Conclusions, implications and outlooks

EPD of C_6H_6 from solid H_2O, CH_3OH and $CH_3CH_2OCH_2CH_3$ surfaces and the formation of H_2 in systems comprising a C_6H_6 adlayer on solid H_2O, CH_3OH and $CH_3CH_2OCH_2CH_3$ have been investigated. We have demonstrated that the C_6H_6 EPD channel is significantly decreased while the H_2 EIC channel is largely enhanced when ices of carbon-bearing molecules are employed during irradiation with 250 eV electrons. The observation that C_6H_6 desorption is less intense while H_2 formation is enhanced in the absence of H_2O is rather noticeable even given the similarities between the C_6H_6/CH_3OH and C_6H_6/ASW ices.[53] H_2 formation and desorption is a common process to the three systems but it is clearly more significant for organic-based ices than in ASW. Ultimately, this striking difference can be addressed by considering the presence of excitations localised around the C-atom *versus* those involving the O-atom with the former favouring reactive routes. Future studies will investigate the nature of the dominant processes occurring during the electron irradiation of organic molecules and how these compare to solid H_2O. This work (i) emphasizes the need to fully understand the distribution of products (branching ratios) of photon- and charged-particle-induced physics and chemistry, (ii) and highlights the importance of looking at the nature of the species leaving the surface and not simply at what remains on and in the ice if we are to incorporate these processes into astrochemical models.

Consistent with the radiolysis of liquids,[59] if it is true that H/H_2 production is likely to be a major process in photolysis and radiolysis of both simple (*e.g.* water-rich) and complex ices (*e.g.* containing COMs), then it is tempting to question to what extent the formation and desorption of H/H_2 can contribute to hydrogen recycling in various environments. For example, early in dense cloud formation, gaseous H is initially depleted on to grains that catalyse H_2O, NH_3, and CH_4 formation. Irradiation of these molecules as icy mantles accrue would promote EIC which on one hand yields radicals and enriches the ice in COMs, but on the other seems to return H_2 to the gas phase, leaving residues that will potentially become increasingly unsaturated and with time probably aromatic. Further experiments, at

temperatures as low as 10 K, are required to reinforce these intriguing speculations.

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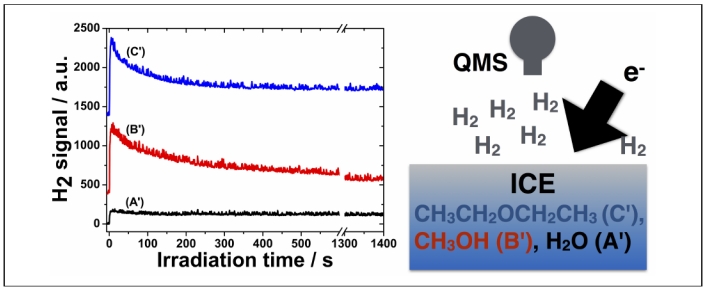
H2 signal / a.u.
Irradiation time / s
(C')
(B')
(A')
QMS
e-
H2
ICE
CH3CH2OCH2CH3 (C'),
CH3OH (B'), H2O (A')